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FC05. 文化遗产材料论坛（国际）

分会主席：王凤平教授、李炫华教授、韩向娜教授、Giuseppina Padeletti Vice present of E-MRS

分会编号-01

我国墓葬壁画的发现与保护

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中国壁画艺术源远流长，各类丰富多彩的壁画是研究中国古代社会政治、经济、宗教、美术、建筑等方面的珍贵实物资料。因此，古代壁画也称之为“墙壁上的博物馆”，极具历史、艺术、科学技术价值。但壁画在经历了漫长的历史岁月过程中，除受到人为因素的破坏外，更遭到自然因素的侵蚀，损坏极为严重，因此壁画保护是中国文物保护领域的重点，也是文物保护中比较复杂的，难度较大的一个分支。墓葬壁画出现并最终形成一种丧葬文化现象是在汉代。汉代墓葬壁画自西汉前期形成以后，不断发展演变并形成了一套非常系统完整的体系，表达了深邃而复杂的信仰和丧葬观念，丰富和发展了中国古代绘画的造型技巧和艺术表现形式，因此墓葬壁画在早期绘画史和思想史上都占有非常重要的地位。本文较为全面系统地梳理了我国目前发现的墓葬壁画，系统总结了墓葬壁画的保护模式及存在的问题。

分会编号-02

脆弱文物加固材料研究及其应用进展------以三星堆遗址出土饱水糟朽象牙为例

陈家昌 [1]，谢振斌 [2]， 王冲 [2]，张良帅 [3]
1.中国文化遗产研究院
2.四川省文物考古研究院
3.河南省文物考古研究院

四川省三星堆遗址出土了大量的古象牙，为考古、古气候、古生物及古地质研究提供宝贵的实物资料，具有极高的研究价值。然而，由于长期的地下埋藏特别是水分侵蚀造成的象牙劣化，使得出土后的象牙伴随着水分的挥发，会发生突变性损毁，产生开裂、剥落、粉化等现象。为此，研发匹配性高、稳定性好且具有可再处理性强的先进加固材料，实现对劣化骨角质文物病害侵蚀的有效控制，是当今各国骨角质文物保护研究中亟待解决的热点问题。本文采用丙烯酸与无机盐反应制备出了丙烯酸盐配合物溶胶材料用于饱水糟朽象牙的加固。加固实验表明：该溶胶具有“有机-无机”微观（介观）复合材料的结构特征，同象牙文物的结构、性能有着良好的匹配性与结合性，含钙配合物溶胶通过与古象牙之间的物理化学作用改变了古象牙的微观结构，加固前后象牙的抗压接强度平均提高了 230%，加固后饱水象牙在失水干燥过程中易发生的崩解现象消失，饱水象牙自然干燥后较好的保持出土时的原有形貌，表明了含钙金属配合物溶胶是一种性能优良的饱水糟朽古象牙加固材料。迄今为止，采用含钙配合物溶胶材料已对十数根象牙进行了加固处理，实现了饱水糟朽象牙整根脱水加固“零的突破”。

分会编号-03

文物保护视野下的纺织材料研究

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纺织材料包括纤维和染料，纤维赋予纺织品实体，染料赋予纺织品颜值。对于纺织品文物而言，对纤维和染料开展符合文物保护原则的材质鉴别、劣化机理、产地溯源都是值得关注的话题。本报告通过实验室的研究与考古案例的应用，着重阐述文物保护视野下的纺织材料研究新进展、新成果。

分会编号-04

南昌市西汉海昏侯墓园实验室考古中的文物保护材料应用研究

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本文以南昌市西汉海昏侯墓园的实验室考古研究为例，从应急保护材料、临时固型材料和加固保护材料三个方面讨论文物保护材料在考古发掘现场出土遗存保护中的应用问题。本研究认为，应急保护材料应满足方便获取、起效快、易去除、不污染遗存的要求；临时固型材料应满足强度高、可去除、不污染遗存的要求；加固保护材料应满足强度高、稳定性强、不影响后期科学分析研究的要求。本研究为考古发掘现场出土遗存保护、脆弱质遗存提取、实验室考古应急保护中的文物保护材料选用提供了借鉴。

分会编号-05

三星堆遗址祭祀区现场应急保护体系与出土象牙的提取保护

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2020 年 10 月，三星堆遗址祭祀区启动新一轮考古发掘，发掘过程努力践行“创新、协调、绿色、开放、共享”的创新发展理念，构建了“课题预设、保护同步、多学科融合、多团队合作”的考古发掘新模式。充分运用现代科技手段，研发了集考古发掘舱、多功能发掘操作系统、应急保护、信息采集管理、微环境控制等为一体的、具有国际领先水平的考古发掘保护平台。发掘过程中针对高含水率糟朽象牙提取难题，筛选评估考古现场常用临时固形材料，解决潮湿环境下象牙提取时间长、固形效果差、提取过程易于损坏等问题，为脆弱文物现场提取、临时固形提供新的方法。

分会编号-06

PEI/PEGDE/IPP 法加固糟朽粉化丝织品文物研究

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1.荆州文物保护中心

丝织品是有机质类文物的重要代表之一，具有极其重要的历史、文化、艺术价值。由于蚕丝纤维是一种蛋白质，容易通过多种途径降解，因此出土的丝织品文物通常都会出现不同程度的糟朽甚至是粉化病害。为了防止蚕丝蛋白进一步劣化，应当解决以下两个关键问题：（i）丝织品文物蚕丝纤维束原位塑形；（ii）加固蚕丝纤维束并保证其柔韧性。另外，还应充分考虑颜色/质地/光泽变化、二次降解风险、技术成本、毒性污染等因素。

针对丝织品文物这一典型的病害问题，通过顺序浸渍，使支化聚乙烯亚胺（PEI）分子与聚乙二醇二缩水甘油醚（PEGDE）分子均匀附着于单根纤维束表面，并利用两者的开环聚合反应形成三维空间自适应的交联网络，包覆糟朽、粉化的蚕丝纤维束，同时诱导丝素蛋白沿（210）晶面有序排列，不仅保持了糟朽、粉化丝织品文物的结构稳定性，而且增强了其强度、韧性、弹性和抗撕裂能力；将棕榈酸异丙酯（IPP）分子引入聚乙烯亚胺/聚乙二醇二缩水甘油醚（PEI/PEGDE）骨架中可以形成有机凝胶基质，从而提高丝织品文物的柔软度和延展性。该方法体系既可以实现丝织品文物的原位加固塑形，有效提升糟朽蚕丝纤维的机械性能，同时抑制粉化病害的发生和蔓延，又保持了丝织品文物原有的颜色和柔韧性，使其原貌得到最大程度地再现。

分会编号-07

Study on the preparation and properties of functional zeolite composite materials for the protection of paper relics

Hongbin Zhang[1]
1. Fudan University

Due to the high historical value and large quantity of paper relics, the protection against their aging and deterioration is an urgent problem in the field of cultural heritage protection. The proposal is to meet the needs of efficient, safe and multiple protection of paper relics. In view of the complexity of anti-deterioration of paper relics and the difficulties faced by existing protective materials, zeolite functionalized composite materials are innovatively applied to the multi-functional protection of paper relics based on the high applicability to paper and the characteristics of adjustable and controllable alkaline, easy selective modification and functionalization. Through the development of new methods of zeolite modification and functionalization that suitable for the paper relic protection, the long-lasting slow-release and safety of alkaline zeolite for paper deacidification can be realized, without negative effects such as alkaline hydrolysis, pigment discoloration and fading. In addition, protection functions such as bacteriostasis, reinforcement, oxidation resistance, light aging resistance, flame retardancy, etc., can be selectively added, so as to solve the protection problems of different paper cultural relics (such as different age, type, degradation degree, etc.) by coordinating and controlling the interaction and influence of various protective agents. Furthermore, we will study the corresponding anti-aging protection mechanism of new materials, deepen the understanding of the synergy and role of various aging degradation mechanisms through the feedback of structure-activity relationship, and further provide a new material system and development ideas for paper relic protection.

分会编号-08

Research on A Novel in-situ Crosslinking Method for Soil Aggregation Reinforcement

Juanli Wang[1]

1. Northwestern Polytechnical University

The relics of the earth site are important cultural heritage left by the ancestors, bearing the information of various historical periods of culture, art, science and technology and so on. However, The most of the earthen sites are affected by the external environment for a long time. The soluble salts have been repeatedly dissolved and crystallized, resulting in the ruins of the sites' structure and threatening the sites' safety. Therefore, the accurate understanding of the influence of water and salt transport inside to the site performance degradation characteristics and the establishment of effective measures to protect process，which have important theoretical and practical significance to effective protection measures and the preservation life of the site. In view of the existing problems in the research of the existing sites for chemical reinforcement of soil, the method of TEOS hydrolysis in situ crosslinking to reinforce soil sites was studied in this paper. Around this method, the hydrolysis conditions of TEOS and the optimization of the remolded soil samples strengthened by TEOS were carried out；water migration behavior of remolded soil samples before and after TEOS reinforcement were studied；water and salt migration behavior of remolded soil samples before and after TEOS reinforcement were studied. Water and salt capillary migration simulation test of soil site was designed, water and salt migration behavior of the remolded soil samples before and after TEOS reinforcement was systematically studied by SEM, LS, MIP, XRD, EDS, conductivity, IC, LOW-HMR and other analytical methods in order to obtain the microscopic action mechanism of the difference of water and salt migration of the remolded soil samples before and after TEOS reinforcement. The relationship between water transport behavior in remolded soil samples and the micro pore structure of soil aggregates was constructed and the mechanism of TEOS in-situ cross-linking on Earthen Site reinforcement and protection was revealed. Finally, the reinforcement effect of TEOS strengthening agent was evaluated systematically from three aspects of apparent, internal pore and overall mechanical properties. It is expected that these results will be instructive for soil erosion control.

分会编号-09

Removal Material of Mildew Stains on Acidified Paper Cultural Relics Surface based on pH-drive Protein

Phase Transition Strategy

Jing Cao[1]
1. Northwestern Polytechnical University

Paper cultural relics are important carriers and physical witnesses for recording and inheriting civilization. Molds are the most widespread harm to paper cultural relics, and the research on mildew removal is crucial to extend their life. In order to overcome the disadvantages of traditional methods of stain removal, such as complex system, tedious steps, and easy to cause damage to cultural relics, this project proposes a new material for the removal of mildew stain on the surface of acidified paper cultural relics based on pH-driven protein phase transformation strategy. It is planned to take the surface interface of acidified paper cultural relics as the in-situ reactor, and take the retained acid detached from the hydrolysis as the driving force of protein phase transformation, so as to realize the removal of mildew stains on the surface of paper cultural relics in a single aqueous environment. Based on the direction and driving relationship between system pH and protein phase transformation, the autocatalytic protein phase transformation process in mild aqueous system is studied. The dynamic change of reaction activity sites is used to explain the evolution process of multiple phase states exhibited by phase transformed proteins in different system pH environments. The evolution law of key action targets of protein conformation with the change of system pH and the matching relationship with mildew functional groups are explored. The mechanism of action between system environment-protein conformation-mold stain is revealed from the molecular level, and the matching "interface adhesion" was realized to target mildew stains removal, which laid a foundation for the development of phase transformation proteins in the cleaning application of paper cultural relics protection.

分会编号-10

Analysis and Reflection on the causes of different diseases in Cave 60 and Cave 94 of Maijishan Grottoes

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1. Maiji Mountain Grottoes

Cave 60 and Cave 94 of Maijishan Grottoes are located in the lower of the west cliff of Maijishan, which have similar elevation and size, although they have different types. It is found that the main diseases of murals and statues in Cave 60 and Cave 94 are different through the investigation. The main disease of Cave 60 is the deep loss, and the main disease of Cave 94 is the deep lose and the alkali. Environment is the main influencing factor of diseases. In order to further clarify the causes of the differences in the main diseases , the environmental data （temperature and relative humidity）of heavy rainfall of 2020 year in the past five years were used as the basis. By comparing the relative humidity variation of monthly average, daily average and the real-time itself before, during and after of heavy rainfall day in 2020 of the out and inside of caves, it is found that the daily average relative humidity in Cave 60 and Cave 94 is greater than 62% all the year round Among them, the relative humidity of Cave 60 changes with the change of external environment, and the fluctuation is more intense, while the relative humidity of Cave 94 fluctuates less. Therefore, it is speculated that the exchange of relative humidity inside and outside is only a part of the factors that lead to the occurrence of alkali in murals and statues of Cave 94, and the moisture of cliff body is the main factor for the continuous stability of high humidity in the cave, and the main external influencing factor for the occurrence of serious efflorescence diseases. Therefore, it is speculated that the exchange of relative humidity inside and outside is only a part of the factors that lead to the occurrence of alkali in the murals and statues of Cave 94, and the water content of the cliff is the main factor for the continuous stability of high humidity in the cave and the main environmental factor for the serious alkali.

分会编号-11

Advanced Discrimination of Pigment Manufacturing Methods Using Deep Learning Techniques

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2. Korea Foundation for the Traditional Architecture and Technology

Analytical techniques have been employed in domestic cultural studies since the 1980s. With the rapid development of industrial technology, research has increasingly focused on material science. Recently, the advent of the Fourth Industrial Revolution has led to the gradual accumulation of research results. This accumulation has facilitated in-depth studies, such as estimating the source of raw materials by applying various statistical analyses to extensive data sets, thus highlighting the importance of multidisciplinary research. In the fields of forestry, botany, and soil science, discrimination and judgment models utilizing image recognition data and artificial intelligence are being developed. However, applying big data analysis methods remains rare, particularly in the mining and cultural heritage sectors, where basic research is still relatively lacking.

This study developed a classification system to discriminate between the manufacturing methods of pigments, the primary raw materials in colored cultural assets. While natural mineral pigments have unique crystal forms and have traditionally been used, artificial synthetic pigments have increasingly replaced them since the Industrial Revolution. By leveraging the unique crystal forms of natural mineral pigments, an AI-based discrimination model using Convolutional Neural Networks (CNN) was developed through the microscopic imaging of pigments.

分会编号-12

Exploratory study of in situ consolidant for fragile organic relics in high humidity environments in archaeological sites

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2. Xi'an Cultural Heritage Promotion Centre

Fragile organic artifacts found at archaeological sites often require consolidation prior to extraction, but there are few or no suitable consolidants available in such high humidity environment. To solve this challenge, a new kind of moisture curable polyurethane (MCPU), as a consolidant for conservation, was specifically designed and prepared. The reaction and consolidation mechanism, appearance, strength, stability, and consolidation effect were studied. FTIR results showed that isocyanate-terminated polyurethane prepolymer was successfully synthesized. During curing process, the prepolymer can react with vapor or hydroxyl groups on the surface of the artifact substrate to form chemical bonding, and more importantly, avoid the problems of whitening and curing difficulties in high humidity environment. The cured MCPU film is colorless and transparent, with higher strength and toughness than that of Paraloid B72. The thermal decomposition of the film is a primary reaction with an activation energy similar to that of Paraloid B72. The fitted equation showed that the prepared films have a life expectancy of about 330 years at room temperature, which far exceeded the optimal standard of 100 years proposed by Feller for the lifetime of heritage conservation materials. After in situ consolidation of fragile organic Zhusi (竹笥) artifacts with MCPU, the deteriorated fibers were bonded together to form a coherent structure, and the filling effect of the agent provided the strength needed for in situ extraction. This moisture curable polyurethane is expected to solve the bottleneck problem of in situ consolidation of fragile artifacts in high humidity environments.

分会编号-13

Consolidation of cultural heritage through nanolime and its based nanomaterials

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1. Northwestern Polytechnical University

Nanolime is currently a promising inorganic material for cultural heritage conservation, having achieved certain effects in the consolidation of murals and stone artifacts. However, it has drawbacks such as long carbonation time, low stability in water, and short antibacterial duration. To address these issues, we have modified its surface with graphene quantum dots, polydopamine, and quaternary ammonium salts, preparing a series of nanolime-based inorganic nanomaterials, such as nano calcium hydroxide/graphene quantum dots and nanolime modified with polydopamine and quaternary ammonium salts. These materials not only enhance the consolidation strength and penetration depth in murals and stone artifacts but also significantly extend the antibacterial time. Therefore, these nanolime-based materials are considered to have good prospects for cultural heritage conservation.

分会编号-14

Single-atomic nanomaterials as radical scavengers for improving the ultraviolet resistance of the painting layer in mural

Wenting Gu[1]

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Mural hold immense historical value as precious legacies left by our ancestors, yet they face significant damage along with archaeological excavations, necessitating urgent protective measures. Nanotechnology has emerged as a promising avenue for the consolidation and preservation of painting layer of mural, offering novel concepts and materials. In this study, we propose an innovative and cost-effective method that uses Mn/CeO_2 with a radical scavenging ability to enhance the protection of painting layer of mural. The resulting nanocomposite demonstrates the potential application of Mn/CeO_2 nanomaterials in shielding mural cultural relics from harmful ultraviolet (UV) rays. The successful development of this nanocomposite marks a significant advancement in mural protection, opening new horizons for the preservation of mural cultural relics.

分会编号-15

基于热机械分析的脆弱有机质文物微损力学测试

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1. 北京科技大学科技史与文化遗产研究院

出土脆弱质文物因长时间降解导致性质严重劣变，现代材料的性能评估方法已无法完全适用。尤其是现有的宏观力学表征方法精确度不足、样品量需求大，难以对力学性能严重劣化的脆弱质进行有效测试，许多必需的力学重复性试验更是难以开展。为此，本文选用饱水考古木质文物、脆弱考古漆膜及纸质文物三种中国典型的脆弱质文物，以热机械分析技术(Thermomechanical analysis, TMA) 为基础，开发了一种微损的脆弱质物理力学测试方法，载荷及位移测试精度分别高达 9.8 μN 和 0.01 μm。尝试利用此方法测定了 “南海 I 号”沉船饱水船板和刘家洼出土考古漆膜的抗弯强度，以及干热、湿热老化竹纸的抗拉强度，并表征了经不同保护材料处理后文物的力学性能变化。测试使用的样品尺寸分别仅为 2 mm×8 mm×0.3 mm 和 15 mm × 2 mm，所需样品总量仅约为传统力学试验机所需试样的 0.5%。结果表明，运用 TMA 方法测试的脆弱质文物力学强度数据符合随降解程度提高而降低的规律，标准差与样品本身均匀性相吻合，能够有效表征文物的保存状态。并且此方法能够对不同保护材料的加固效果进行定量评估，在保护方法的筛选和研发方面亦有应用前景。

分会编号-16

考古出土秦兵马俑及相关文物的保护修复研究
——材料、历史与艺术的融合

容波[1]

1. 秦始皇帝陵博物院

秦始皇陵及兵马俑坑，南依骊山、北临渭水，被誉为“世界第八大奇迹”，在世界文化遗产中占有重要地位。秦始皇帝陵是中国古代规模最大、结构最复杂、埋藏最丰富的帝王陵墓，是“世界最大的考古学储备之一”，是 2200 多年前人类智慧和劳动的结晶，是我国第一批全国重点文物保护单位和首批世界文化遗产，兵马俑是二十世纪世界上最伟大的考古发现之一，是中华民族的骄傲和宝贵财富，是中华文明的精神标识，具有重要的历史、科学和艺术价值。考古发掘出丰富多彩的秦兵马俑、青铜器、石铠甲等文物，不仅是解读历史的重要线索，也是研究古代材料生产加工技术的实物，更是保护、传承和弘扬古代文明的重要载体。报告以文物材料价值认知、制作工艺、病害机理、保护修复等角度直观明晰地梳理了秦兵马俑考古发掘、彩绘保护、遗迹提取等研究的历程，多学科视野下解读秦俑颜料、工艺特点、遗产价值，领略神秘而震撼的大秦帝国风采。

分会编号-17

彩绘文物中有机颜料的谱学分析

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颜料是古代壁画材料的重要组成部分，它承载着壁画的丰富图像内容和色彩信息。人们对古代壁画颜料的认知大多以具有鲜艳色彩和良好稳定性的无机矿物颜料为主，而忽略了可能在古代壁画中使用的有机颜料。我们通过现场调查和实验室研究，建立了一套古代彩绘文物有机颜料的光谱和质谱分析方法体系，并利用该方法体系在新疆克孜尔石窟、森木塞姆石窟、阿斯塔纳墓葬出土彩绘俑、陕西墓葬壁画中发现了紫胶、黄檗、靛蓝、藤黄等有机颜料，在近代套印木刻年画中发现了龙胆紫、碱性品蓝和碱性品绿等合成有机颜料。另外发现紫胶不仅作为红色颜料在壁画上大面积使用，还用作壁画贴金箔的胶粘剂；而在克孜尔石窟和森姆塞姆石窟还发现了大量贴锡箔装饰，并通过原位质谱成像方法揭示了锡箔表面“仿金”的技法。结合文献记载，我们认为紫胶这种昆虫来源的有机材料来源于印度，它的传播和使用与佛教在新疆的传播和兴盛密切相关，而黄檗等则可能来源于中原地区。这些研究结果为丝绸之路沿线的贸易交流和文化交融提供新的物质佐证，并为光谱和质谱新方法在文物材料中的应用提供了新的思路。

分会编号-18

Multi-technique analysis of wall paintings and polychrome sculptures pigments in Chinese grotto temples

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The Chinese cave temple is an immortal masterpiece of exchanges and mutual learning between ancient civilizations in the world, and a unique carrier and great witness of the integration of multiple cultures. The wall paintings pigments and painting techniques of the grotto temples have distinctive characteristics of the times, contain rich information on history, science and technology, art, etc., and have extremely important research value. Caves 1, 4 and 18 of Tiantishan Grottoes were originally built in the Northern Liang period, fragments of wall paintings from the three caves have been analyzed with a combined approach of Raman spectroscopy, X-ray fluorescence spectrometry, fiber-optic reflectance spectroscopy, and digital microscopic analysis in order to determine the chemical composition of paint pigments. Through a complementary analysis of the molecular composition and microstructure of the pigments, 16 types were successfully identified, 2 of which have never been discovered before. Caves 257 and 259 of the Mogao Grottoes are important caves from the Northern Wei Dynasty. In order to explore

scientifically the artistic characteristics and development process of the wall paintings and polychrome sculptures in these two caves, in-situ non-destructive analysis techniques such as ultra-depth-of-field microscope, fiber optics reflectance spectroscopy, Raman spectroscopy, as well as laboratory analysis techniques such as X-ray diffraction, scanning electron microscope, pyrolysis-gas chromatography/mass spectrometry, etc. are used to study the painting techniques and materials characteristics comprehensively. The results show that the ground layers of the murals and sculptures can be divided into two categories: red and white. The pigments used in Cave 257 include gypsum, talc, red ochre, vermilion, insect-based anthraquinone dye, atacamite, lapis lazuli, indigo, and carbon black. The pigments used in Cave 259 include talc, serpentinite, red ochre, azurite, and atacamite associated with azurite. The research results show that the combination of multiple analytical methods is highly accurate in identifying the majority of inorganic pigments and dyes, and that the nondestructive analytical methods are effective in identifying both pure and mixed pigments. The analytical results also explain the inheritance and evolution of the painting materials in the caves from the aspects of time and space, and provide important support for the archaeological, art historical research, as well as the protection and restoration of the grottoes.

分会编号-19

Identification of the dyes and pigments in different materials of cultural relics preserved in the Palace Museum

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1. 故宫博物院

The brilliant colors on the cultural relics attached higher historical, artistic and scientific value to them. Investigations on the origin of pigments and dyes can not only reveal the dyeing techniques of ancient civilizations, but also help clarify the development of science and technology during the ancient times. The Palace Museum has a collection of 1.8 million cultural relics, and the analysis of the color origin of typical cultural relics can provide an important scientific basis for the judgment of the age of cultural relics, as well as their protection and restoration. Using non-invasive and micro-invasive analytical methods, such as Raman spectrometry, Surface-Enhanced Raman spectroscopy and liquid chromatography combined with mass spectrometry, different pigments and dyes could be identified in cultural relics of different materials. As a result, dyes of natural and synthetic origins were found in the textiles; inorganic and organic pigments were both found in paper-based relics; natural dyes also appeared in the woodwares; multiple inorganic pigments were found in ivory objects. These results could contribute to the ancient handcraft study for the specific materials of cultural relics.

分会编号-20

Exploration of Mural Craquelure and Flaking Characterization and Quantification Techniques Based on Fluorescence Stress Probe

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Ancient murals are a valuable part of China's historical and cultural heritage, frequently harmed by structural defects such as craquelure and flaking, which severely affect their preservation. However, current mechanistic studies are mostly limited to qualitative discussions, and there is a lack of techniques for characterizing, quantifying, and monitoring these defects, especially in-situ non-destructive analysis methods that urgently need to be developed.

Fluorescence stress sensing technology is an emerging and rapidly developing method. Mechanoluminescent or mechanochromic luminescence materials exhibit changes in optical properties under stress, enabling the in-situ, non-contact, and non-destructive detection of stress location and quantification in engineering structures. This study

is the first attempt to apply fluorescence stress sensing technology to the field of cultural heritage conservation, exploring the mechanisms of cracking and flaking ailments.

Based on the fluorescence phenomenon of 1,1,2,2-tetrakis(4-nitrophenyl)ethene (TPE-4N) under stress, this study established a method for tracking and quantifying damage in simulated mural samples in the laboratory. By coating the sample surface with a 0.3g/mL TPE-4N/chloroform solution to create an appropriate thickness of the sensing material layer, micro-cracks generated under accelerated conditions of temperature cycle, humidity cycle, and temperature-humidity cycles could be clearly observed under ultraviolet light in the early stages of expansion. Through photographic recording and monitoring, combined with ImageJ software to quantify crack length, the process of cracking and flaking defects can be quantified.

By comparing the types, severity, and crack propagation characteristics of defects under different accelerated aging conditions, this study confirmed that higher adhesive concentrations significantly accelerated crack propagation, resulting in more severe structural ailments, while environmental humidity had a greater impact on sample deterioration than temperature. In terms of craquelure dynamics, the experiment found that the development of structural ailments in samples underwent an induction period, a stable development period, and a saturation period.

This exploratory study established a quantitative monitoring method for craquelure and flaking defects of wall-paintings in the laboratory, revealed the influences of internal and external factors, and demonstrated the advantages and application prospects of fluorescence stress probe in the mechanistic study of cultural heritage defects. Future work will focus on optimizing probe materials and combining them with protective materials, aiming to adhere to the principles of cultural heritage conservation and expand the scope of application.

分会编号-21

Study on the theory and method of identification for material component of cultural relic based on in-situ nondestructive measurement

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The identification of the material components of cultural relics is a critical aspect of archaeological research and heritage conservation. Traditional methods often involve invasive sampling, which can lead to irreversible damage to these irreplaceable artifacts. In response to this challenge, the development of in-situ nondestructive measurement techniques has revolutionized the field of cultural heritage science. This study aims to explore the theoretical foundations and practical methodologies of material identification for cultural relics using in-situ nondestructive measurement techniques. Raman spectroscopy, as a "fingerprint spectrum," offers a non-destructive characterization method for artifact analysis with its rapid, non-invasive, and micro-analytical capabilities. The use of Raman spectroscopy has already yielded a wealth of information on cultural heritage both domestically and internationally. This article presents a case study on the ancient painted murals of the Beijing Temple of Agriculture and the Yanshan Temple in Shanxi. Portable Raman spectrometers and handheld XRF spectrometers were employed for in-situ non-destructive analysis, successfully identifying the material composition of pigments used in these cultural relics.

Within the Altar of Agriculture complex, this study selected the colored paintings in the Sacrificial Storehouse and the Precious Clothing Hall as research objects, conducting in-depth analysis on the original paintings, restored paintings, and repainted paintings. In the colored paintings of the Sacrificial Storehouse, the use of various pigments such as red lead, lead white, indigo, carbon black, and atacamite were revealed in the original paintings, while modern pigments such as bright red β-naphthol, Sudan I, chrome yellow, titanium dioxide, ultramarine, and phthalocyanine green were detected in the repainted paintings. Notably, chrome yellow, ultramarine, and phthalocyanine green were used for the restoration of the green and blue areas in the restored paintings. As for the

colored paintings in the Precious Clothing Hall, traditional pigments such as cinnabar, red lead, white lead, atacamite, and indigo were used in the original paintings, while ultramarine and Emerald green were used for presenting the blue and green areas in the restored paintings. Multiple modern synthetic pigments including titanium dioxide, chrome yellow, Sudan I, phthalocyanine green, ultramarine, and bright red β-naphthol were identified in the repainted paintings, giving them a new artistic appearance.

The murals of the Yanshan Temple reflect the social life during the Song and Jin dynasties, holding significant importance for researching the social history, religious culture, and architectural features of that period. The study discovered the use of pigments such as cinnabar, red lead, calcium carbonate, gypsum, anhydrite, lead sulfate, carbon black, chrome yellow, azurite, malachite, and chromium oxide in the murals. Among them, calcium carbonate and gypsum were considered as ground layer materials. Lead sulfate was detected in the grayish-purple and red areas, along with red lead. It is speculated that lead sulfate is the degradation product of red lead. Chromium oxide found in one dark green area is a modern pigment synthesized in the early 1800s. Therefore, it can be inferred that this dark green area has been restored in modern times.

Through this research, it was revealed that most of these precious paintings have undergone varying degrees of restoration. Some only required minor repairs in small areas to fix flaws or damages in the artwork. However, some paintings have undergone extreme modernized repainting. Restoring ancient artifacts without detailed knowledge of the original pigments can be highly detrimental to their preservation and study. These investigations not only unveil the material composition of the pigments used in the paintings but also provide valuable information for the preservation, restoration, and study of cultural relics. The application of in-situ non-destructive measurement techniques ensures that we can explore history while maximizing the protection of these irreplaceable cultural heritage.

分会编号-22

无损分析技术在文物保护中的应用

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目前，无损分析技术已成为检测陶瓷、金属、石质、纸张和丝制品等不同材质文物的制作工艺和保存现状的一种有效手段，在文物保护研究中得到了广泛的应用。常用的无损分析仪器有 X 射线衍射仪(XRD)、X 射线荧光光谱仪(XRF)、激光诱导击穿光谱仪(LIBS)、拉曼光谱仪(RS)等。XRD 可以对文物本体以及病害成分结构进行定性和半定量分析。XRF 可以无损分析文物的元素组成，对文物病害的检测起到借鉴作用。LIBS 可检测 XRF 不能检测的锂、碳等低原子序数元素，对文物进行深度和剖面分析。RS 可从物相结构上分析文物组成，判断劣化情况，评估保护效果。本文就无损分析技术在文物保护领域的应用进展进行总结，希望能够为考古从业人员带来有效的参考依据。

分会编号-23

海洋出水瓷器表面典型生物沉积认知

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海洋出水瓷器表面生物沉积现象显著，常见藤壶、贝壳、苔藓虫和盘管虫等大型底栖生物的紧密附着，使得瓷器打捞出水后的表面清洗和保护工作极具挑战性。本研究选取东海圣杯屿沉船遗址出水的一件龙泉青釉瓷碗，对其上的典型底栖生物群落进行了多角度的科技分析。研究应用超景深三维视频显微镜（OM）、扫描电子显微镜-能量色散 X 射线光谱仪（SEM-EDS）、拉曼光谱、傅立叶变换红外光谱（FTIR）和热重分析等手段，研究了不同类型生物结核的微观结构、化学组成及其在釉面上的固着形式，初步评估了其对釉层的侵蚀程度。研究结果揭示了出水瓷器表面典型生物沉积病害的形成机制和附着机制，为未来提出安全

有效的清洗去除手段提供了新的依据和支撑。

分会编号-24

Nondestructive Spectroscopic Analysis of Pigments in the Architectural Polychrome Paintings of Prince Kung's Palace (Beijing, China)

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4. Institute of High Energy Physics, Chinese Academy of Sciences

5. The Palace Museum

In this study, the portable Raman spectrometer and X-ray fluorescence spectrometer (XRF) were used to conduct comprehensive in-situ nondestructive analysis of the colored paintings in Prince Kung's Palace architectural complex, which is the largest palace of a prince in the Qing Dynasty (1644–1912 CE). Due to the several changes in ownership of the Prince Kung's Palace, the colored paintings within have also been altered accordingly. This study focused on eight typical colored paintings of Prince Kung's Palace and has successfully identified the pigments used. The results indicate that the pigments in these exquisite colored paintings consist of mineral pigments commonly used in ancient times and modern synthetic pigments. Among them, the mineral pigments include cinnabar, red lead, hematite, orpiment, lead white, calcium carbonate, carbon black, azurite, and atacamite; Synthetic pigments comprise Hansa red, chrome yellow, titanium dioxide, Prussian blue, ultramarine blue, phthalocyanine blue, emerald green, and phthalocyanine green. In addition, the plant pigment indigo is also found in localized areas. Meanwhile, some pigments may be degenerate products, such as lead sulfate and gypsum. The use of different pigments within the same hue suggests varying periods of creation for the paintings and reveals the historical restoration of the colored paintings in Prince Kung's Palace from early times to the present. Based on the analysis of pigments used and the architectural history, the earliest colored paintings in the Prince Kung's Palace can be traced back to around the 45th year of the Qianlong reign (1780 CE), while some may have been created during the period of the Republic of China (1912–1949 CE). The research on the pigments of the colored paintings in the Prince Kung's Palace, sheds light on the historical and cultural context of the palace and provides important guidance for the preservation and restoration of the colored paintings in the Prince Kung's Palace.

分会编号-25

明清官式建筑油饰彩画地仗粘结材料的改性研究

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油满是明清官式建筑油饰彩画地仗层的主要粘接材料和常用修复材料，主要有熟桐油、面粉和石灰水混合调制而成。油满不仅符合文物修复材料的兼容性原则，还具备粘接能力强、可操作性好等优点，对建筑油饰彩画的保护与修复具有重要作用。但另一方面，油满也存在干燥时间长、不耐老化等明显缺点，亟待对其进行科学改性。

因此，本研究以传统油满为研究对象，分别针对油满的干燥时间和耐候性两方面对其进行科学改性，开发一种干燥速度快、耐候性优异且适用于建筑油饰彩画保存与修复的新型油满材料。

干燥时间方面，本研究选用金属催干剂、光引发剂和异氰酸酯等材料对传统油满进行科学改性。研究结果表明，TDI（甲苯二异氰酸酯）改进传统油满的干燥时间的效果最好，当 TDI 的添加量达到 2.00%时，油满的实际干燥时间缩短到 2.50 h，较传统油满实际干燥时间缩短了 68.75%。

热膨胀系数方面，本研究选用砖灰、二氧化硅和膨润土等材料对传统油满进行科学改性。研究结果表明，膨润土和二氧化硅降低传统油满的热膨胀系数的效果最好，当添加量达到 40.00%时，膨润土和二氧化硅分别令传统油满的热膨胀系数降低 55.19%和 48.15%。但膨润土显著提升了传统油满的吸湿性能，可能不利于油满在高湿环境下的保存与使用，故本研究将膨润土与二氧化硅两种材料进一步复配，在降低传统油满与木质基底热膨胀系数差异的基础上令油满保持较低的含水率。

对三种配方改性油满进行了系统性评价和耐候性对比考察。研究结果表明，三种配方改性油满在干燥速度、热膨胀系数等方面较传统油满有较好提升，且温度循环老化实验 100 d 后，三种配方改性油满均未出现结构性病害。温湿度循环老化实验 100 d 后，1 号配方改性油满出现龟裂等结构性病害，推测主要原因为膨润土增加了油满与木质基底湿膨胀系数的差异，导致油满材料收到破坏。2 号配方和 3 号配方改性油满经温湿度循环老化实验 100 d 后未出现明显结构性病害，耐候性更好。

综合上述结果，本研究确定最佳改性油满配方 2 号配方：添加 2.00%TDI 和 40.00%二氧化硅；实际干燥时间 2.00 h，较传统油满缩短 75.00%；热膨胀系数 10.008×10^{-5} m℃-1，较传统油满减小 48.69%；温度循环和温湿度循环老化实验 100 d 后，均未出现明显结构性病害；现场应用示范 60 d 后，整体效果良好。

本研究较好解决了传统油满干燥时间长和耐候性差的问题，成功开发一种干燥速度快、耐候性优异且适用于建筑油饰彩画保存与修复的新型油满材料，有望于官式建筑油饰彩画的保存与修复中推广使用。此外，本研究利用静态热机械分析仪（TMA）首次测出油饰彩画地仗层粘接材料油满及木质基底的热膨胀系数，为油饰彩画结构性病害机理提供了科学证据。在此基础上，本研究尝试从减小传统油满与木质基底热膨胀系数差异的角度尝试改进传统油满的耐候性并取得了良好效果，可为后续油饰彩画结构性的病害机理及保护研究提供参考。

分会编号-26

Co-Self-Assembled Monolayers Modified NiOx for Stable Inverted Perovskite Solar Cells

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[4-(3,6-dimethyl-9H-carbazol-9yl)butyl]phosphonic acid (Me-4PACz) self-assembled molecules (SAM) are an effective method to solve the problem of the buried interface of NiOx in inverted perovskite solar cells (PSCs). However, the Me-4PACz end group (carbazole core) cannot forcefully passivate defects at the bottom of the perovskite film. Here, a Co-SAM strategy is employed to modify the buried interface of PSCs. Me-4PACz is doped with phosphorylcholine chloride (PC) to form a Co-SAM to improve the monolayer coverage and reduce leakage current. The phosphate group and chloride ions (Cl−) in PC can inhibit NiOx surface defects. Meantime, the quaternary ammonium ions and Cl− in PC can fill organic cations and halogen vacancies in the perovskite film to enable defects passivation. Moreover, Co-SAM can promote the growth of perovskite crystals, collaboratively solve the problem of buried defects, suppress nonradiative recombination, accelerate carrier transmission, and relieve the residual stress of the perovskite film. Consequently, the Co-SAM modified devices show power conversion efficiencies as high as 25.09% as well as excellent device stability with 93% initial efficiency after 1000 h of operation under one-sun illumination. This work demonstrates the novel approach for enhancing the performance and stability of PSCs by modifying Co-SAM on NiOx.

分会编号-27

Conservation of the weathered gypsum mortar in historic constructions using hydroxyapatite protectant: the exploration of the new strategy

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Gypsum mortar in the historic constructions is easy to be corrode by the natural precipitation or in the wet

environment. A conservation method using hydroxyapitite as consolidant was explored in this study. The strategy is introducing the solutions of calcium hydroxy glycolate and diammonium hydrogen phosphate (DAP) into the weathered gypsum mortar one by one. As a novel calcium source, calcium hydroxy glycolate is characterized by high solubility and permeability. The reaction between calcium hydroxy glycolate and DAP can generate the continuous mineral phase of hydroxyapatite, which can play the roles of both surface protection and integral reinforcement. XRD, FT-IR, and SEM-EDS were employed to study the action mechanism of the consolidant. The mechanic strength, water erosion resistance, compatibility, and weather ability testing were to investigate the protective performance. The highly positive results show that the proposed method is promising in the conservation of the weathered gypsum mortar in historical buildings.

分会编号-28

海洋出水木质文物中铁质沉积物的研究进展

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铁质沉积物的生成在海洋环境中是非常普遍的现象。海洋考古木质文物中铁质沉积物问题早在上个世纪八十年代就有零星报导，但由于大型木船的保护主要从 20 世纪 60 年代开始，在此期间，铁质沉积物的影响尚处于潜伏期，因此并没有引起特别广泛的关注。自 2000 年起，著名的瑞典沉船 Vasa 号出现了白色或黄色盐析的现象，经分析主要成分为黄钾铁矾、绿矾、石膏、硫单质等；同时伴随有船体木材的酸化，pH 值低于 3，局部甚至低于 1。研究表明这些现象发生的主要原因是木材中沉积的硫铁化合物在空气中发生了氧化，生成硫酸以及各种含铁化合物，而这一过程如不控制最终将导致船体本身崩解。随后更为广泛的研究表明，国内外的海洋考古木船，如英国的 Mary Rose 号、澳大利亚的 Batavia 号、意大利比萨的古罗马沉船、中国的南海 I 号，华光礁 I 号、小白礁 I 号、泉州湾宋代海船等都有大量的铁质沉积物存在。可以说，铁质沉积物已经成为威胁海洋考古木质文物，特别是木船的重要因素。

此前的研究表明，海洋近海表面富含氧气，有机质的腐败消耗氧，当氧消耗殆尽时（$[O_2]<10^{-6}$mmol/L），就形成了低氧或无氧环境。在这种条件下，微生物在新陈代谢过程需要利用其他化合物代替氧作为电子受体。海水中的硫酸盐还原菌在代谢有机物过程中，以硫酸盐作为电子受体，使之还原成硫化物，继而与海水中溶解的 Fe^{2+} 反应生成铁的硫化物。木船打捞出水后，还原态的铁质沉积物在有水存在时极易发生氧化，生成硫酸，促进木材中本已受到破坏的纤维素发生进一步降解。其次，Fe^{2+}/Fe^{3+} 催化的芬顿反应会导致木材有机质和填充加固材料的降解。另外，铁质沉积物氧化后形成的盐单位分子体积发生膨胀，一旦失水析出，会对纤维产生应力破坏。最后，木材中的单宁、酚类物质极易与铁发生反应，导致木材颜色变深，影响文物的外观。硫铁化合物引起的木材酸化问题的解决方法主要有三种思路：第一种是采用甲基碳酸镁水溶液、脲和氢氧化钠酒精溶液、倍半碳酸钠溶液等碱性试剂中和生成的酸，第二种是采用螯合试剂（乙二胺四乙酸等）与铁离子形成稳定的配合物，去除铁离子。第三种是采用聚合物将硫铁化合物包裹起来，延缓其氧化反应。

近些年，关于海洋考古木质文物中的铁质沉积物开展了大量的研究，在铁质沉积物的形成过程、铁质沉积物的存在形式、铁质沉积物的危害及作用机理、铁质沉积物的脱除与控制方法、铁质沉积物脱除与控制过程对于木材本体的影响等方面取得了一些新的进展。

海洋出水木质文物在水下埋藏过程中，在氧化环境中，赤铁矿是稳定的矿物。在还原的环境中，稳定的铁矿物可以是黄铁矿、菱铁矿或磁铁矿。当环境周围的硫不足以与铁反应的时候，铁就处于弱还原环境中，形成磁铁矿、菱铁矿。打捞出水之后，海洋考古木材中的铁质沉积物有三种存在形式：硫铁化合物、氧铁化合物和含铁的盐。硫铁化合物包括黄铁矿、白铁矿、胶黄铁矿、硫化亚铁等；铁氧化合物包括针铁矿、纤铁矿、赤铁矿、磁铁矿；含铁的盐包括黄钾铁矾、钠铁矾、菱铁矿、草酸铁、绿矾等。这些铁质沉积物的存在形式随木材在海底埋藏过程中与铁接触的程度、木材打捞出水后与氧接触的程度发生变化，存

在多价态的中间产物，但总体的变化次序应当是随着木质文物打捞出水，在水和氧的作用下，还原态的硫铁化合物，如黄铁矿、胶黄铁矿等逐渐转化为中间价态的硫和铁，最终会氧化生成氧化态的硫和铁，如赤铁矿、纤铁矿、针铁矿、黄钾铁矾等。

铁质沉积物导致木材降解的机理如下：二价铁与环境中的氧反应，生成三价铁和氧自由基，氧自由基在酸性条件与二价铁反应，生成过氧化氢。过氧化氢与二价铁组成芬顿试剂，氧化木材中的纤维素、木质素和填充加固的有机材料。

除络合试剂乙二胺四乙酸、二乙三胺五乙酸、乙二胺-二（2-羟基-4-甲苯基乙酸）等被用于去除木材中的铁质沉积物外，肌酸六磷酸钙、柠檬酸铵等水溶性的螯合剂也被用于铁的脱除。此外还试验了在络合试剂中加入过硫酸钠、过氧化氢等氧化试剂或抗坏血酸等还原试剂的方法，使铁更快地从木材中迁移出来。此外电泳方法、氧化亚铁硫杆菌处理的微生物方法也被试验性地用于铁的脱除。

采用红外光谱、核磁碳谱等方法考察 L/H 比（木质素/综纤维素）、测定木材含水率、基本密度、动态热机械性能的变化等用于考察络合试剂对于木材本体的影响。

关于海洋出水木质文物中的铁质沉积物未来仍有诸多问题需要解决。如更高效的脱铁材料和工艺、残余的铁对于木材的影响、残余铁的情况下木质文物的保存条件等。只有开展充分研究才能保证我国海洋考古木船、小型木质文物，乃至其他有机质文物的长期稳定性保存。

分会编号-29

Assessment of the Impact of Desalination, Corrosion Inhibitors, and Coating Materials on Iron Cultural Relics through Oxygen Consumption Measurement

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The corrosion and deterioration of iron cultural relics primarily result from the oxidation of iron substrate or ferrous compounds by atmospheric oxygen. Measuring the rate of oxygen consumption offers a means to gauge the corrosion and deterioration rate, reflecting the chemical stability of these relics. Additionally, it allows for evaluating the efficacy of conservation materials and methods. In this study, rusted iron sheet samples containing chlorides were subjected to assessment using five desalination solutions, two corrosion inhibitors, and four coating materials, measured via oxygen consumption. An iron stirrup underwent testing across various conservation treatment stages. Results indicate desalination as the pivotal step, significantly enhancing relic stability, with 0.1mol/L NaOH emerging as a suitable desalination solution. While various corrosion inhibitors and coatings showed promise in improving relic stability, their application should follow successful desalination. The stability of the iron stirrup progressively improved post-desalination, corrosion inhibition, and coating. Portable oxygen consumption measurement equipment is recommended due to its ease of use and suitability for diverse relic types. Compared to traditional weight methods, it offers heightened sensitivity and is unaffected by rust product shedding, promising a more substantial role in the conservation of iron and metal cultural relics moving forward.

分会编号-30

Study on the Embrittlement Mechanism of Sanxingdui Excavated Gold Masks Based on Scanning Electrochemical Cell Probe Technique (SECCM)

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The Sanxingdui gold masks are highly precious historical artifacts that offer crucial insights into the development of the ancient Shu civilization, thereby enriching our understanding of prehistoric Chinese civilizations. By studying the composition, structure, and production techniques of the Sanxingdui gold masks, we not only showcase the exceptional metallurgical and artistic skills of the ancient Shu people but also reflect their profound religious beliefs and cultural traditions. These gold masks are not just artistic treasures but also serve as testimony to the wisdom and faith of ancient peoples.

However, the Sanxingdui gold masks face a severe embrittlement issue, greatly affecting the continuity of the material life of these artifacts. Considering that embrittlement issues (intergranular corrosion) in gold and gold alloys are rare, there has been no systematic and scientific understanding and research conducted by scholars. Meanwhile, corrosion-sensitive microstructures within the artifacts still exist, posing a risk of continued corrosion and degradation during subsequent museum preservation processes. Therefore, research on the embrittlement mechanism and protective measures is urgent and necessary.

Building upon previous researches by our team on the intergranular corrosion mechanism of archaeological silverware, corrosion-resistant materials, and the design of ultramicroscopic probes, this study utilizes scanning electrochemical cell microscopy (SECCM) technology. At the microscale, we quantitatively characterize the electrochemical behavior (thermodynamic + kinetic processes) of the gold-silver continuous phase, the intermetallic compounds Au_2Pb and $AuPb_2$, within the matrix of the Sanxingdui gold masks, aiming to elucidate their corrosion processes and mechanisms. From a corrosion thermodynamics perspective, the corrosion sequence of microstructural components in the Sanxingdui gold mask matrix is $AuPb_2$ phase (greater than) Au_2Pb phase (greater than) gold-silver continuous phase. From a corrosion kinetics perspective, the initial corrosion rates follow the sequence of $AuPb_2$ phase (significantly greater than) Au_2Pb phase (slightly greater than) gold-silver continuous phase, ultimately presenting a trend of intergranular corrosion, leading to localized embrittlement of the gold masks.

分会编号-31

Research on Corrosion Inhibition Treatment of Rusty Bronze Ware by MBT/Na2MoO4/ $CHN_2Na_2O_8$ Organic inorganic hybridization Systems and their Complex Corrosion Inhibition Mechanism

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Bronze cultural artifacts are precious cultural heritage of ancient China. After thousands of years of vicissitudes, their surface has grown rust layers of blue and green colors, deepening their artistic and cultural value. However, after the excavation of bronze wares, their contact with O_2 and H_2O in the air atmosphere will accelerate corrosion, especially when there are "harmful rusts" on the surface such as chlorocopper [$Cu_2(OH)_3Cl$] and hydroxychlorocopper [$CuCl_2 \cdot 3Cu(OH)_2$], which poses a threat to the protection of bronze wares. In this work, 2-mercaptobenzothiazole (MBT) and sodium molybdate (Na_2MoO_4) / disodium ethylenediaminetetraacetate ($CHN_2Na_2O_8$) were successfully applied in the corrosion protection of rusted bronze samples. The effect of corrosion inhibitors on the corrosion resistance of bronze ware was studied through SEM, EDS, XPS, and electrochemical methods, further exploring their synergistic corrosion inhibition mechanism on the rust layer of bronze ware.

Firstly, mixed rust was prepared on the surface of bronze specimens by constant potential deposition method. Its main components were CuCl, Cu_2O, $Cu_2(OH)3Cl$, $Cu_2(OH)_2CO_2$, which appeared light green at the macro level (L=66, a=-12, b=4). At the micro level, the rust layer had a loose porous structure. After soaking with MBT/Na_2MoO_4/$CHN_2Na_2O_8$ corrosion inhibitor for 30 min, the macroscopic color of the rust layer remained basically unchanged (L=67, a=-11, b=4), and the number of pores at the microscopic level decreased, making it denser compared to before treatment.

Secondly, the Tafel results shows that the corrosion resistance of bronze specimens after corrosion inhibition treatment is significantly improved, with a corrosion potential (Ecorr) 0.34 V higher than that of untreated specimens,

a decrease of 2 orders of magnitude in corrosion current density(icorr), and an increase of 83 times in polarization resistance (Rcorr). Moreover, the EIS results indicate that the outer layer resistance of the bronze specimens significantly increased after corrosion inhibition treatment, while the inner layer resistance changed less, which was consistent with the microscopic changes in rust density.

Besides, the CV curve indicates that the oxidation-reduction peak of the specimens weakened after corrosion inhibition treatment, which may be due to the reaction between MoO_4^{2-} and PO^{3-} and the copper substrate, blocking the contact oxidation between the metal matrix and corrosive medias (H_2O and O_2), and improving the polarization degree of the metal interface. The XPS results demonstrate that MBT is chemically adsorbed on the surface of the rust layer, and it may form a dense protective film by complexing with the plasma of $\equiv Cu^{2+}$and $\equiv Sn^{2+}$, which improves the corrosion resistance of the rusted bronze sample.

In summary, the corrosion inhibitor MBT/Na_2MoO_4/$CHN_2Na_2O_8$ adopts a combination of inorganic and organic compounds, while utilizing physical adsorption, chemical adsorption, and redox reactions to form a composite films, of which the synergistic effects enhance the corrosion inhibition effect on bronze wares, greatly improving their corrosion resistance in existence environment.

分会编号-32

The technique of red painting for bronze artifacts unearthed at Sanxingdui Sites

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Many painted bronzes have been excavated from sacrificial pits at Sanxingdui. This article provided a scientific analysis of the painted pigments and the process of applying colors, which helped to explore the technique of ancient bronze decoration. The painted sample collected from a bronze statue which had tiger head and dragon body. Optical and electron microscopy were used to determine the layering state of its painted. The combination of micro-Raman and EDS clarified that the red pigment was cinnabar. In the application of BCA protein test, high-performance liquid chromatography-mass spectrometry (LCMS) and gas chromatography-mass spectrometry (GCMS), it was clear that the painted cementing material was lacquer, not animal gelatin. Taking the overall data into account, the red lacquer in the grooves of the bronze artefacts was applied by a multi-layer coating process. The bronze surface was firstly coated with lacquer and then filled with cinnabar to apply the colors before the lacquer was fully solidified. For the grooves being full of painted decoration, the cinnabar and lacquer layer was coated layer by layer. The cinnabar particles should be squeezed properly to be fixed in the lacquer, and part of the cinnabar was embedded in the lacquer. This exploration and conclusion can help to clarify the decoration process of the bronze at Sanxingdui and promote the study of the technique and evolution of ancient metal painting.

分会编号-33

A quantitative approach to search for structure in cultural heritage

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1. Sun Yat-sen University

This talk follows the work of a world-renowned metallurgist and historian of metallurgy Professor Cyril Stanley Smith (1903-1992), who pioneered the use of solid-state physics in the study of ancient art and artifacts to reconstruct their cultural, historical and technological significance. He proposed the concept of Structural Hierarchy to qualitatively describe the structure of materials and the structures underlying art and history. For materials, "hierarchy" refers to the interlocking of the smaller parts that generate the larger overarching structures. For a work of art, the word "style", which is also hierarchical according to Smith, refers to the unique quality that depends on the way in which its component parts are shaped and put together. Smith did urge museum metallographers to use

quantitative methods wherever appropriate, for example, grain size and volume fraction of a given constituent. However, the structure of a material itself consists of a system and thus deserves a systematic approach for quantification. Unfortunately, the same low-level statistical measures mentioned above by Smith are still widely used today. Based on the latest progress on understanding the mathematics behind deep machine learning, Huang (the first author) proposed the MicroStructural Hierarchy Descriptor (μSHD) in 2022 using the Mallat Scattering Transform, which matches both the physics and mathematics behind the structure of a material. This talk therefore adopts μSHD as a quantitative tool to reexamine the microstructures of metallic artifacts qualitatively described by Smith, which include the famed sword of Damascus from the 18th century, the cast bronze vessel from the Zhou dynasty, the copper chisel from Iran (ca. 3000 B.C.), and ancient silver and silver alloys. Quantitative rather than qualitative descriptions on the internal structural details of the artifacts will be presented and discussed, which can significantly facilitate comparisons among artifacts sharing similar structures with nuance differences, and thus help to better understand the recorded human history, reflecting man's skills and knowledge. The μSHD approach is also applicable to work of art, such as landscape paintings, ancient Chinese characters, ancient calligraphy, etc. As an example, the quantitative differences between the "styles" hidden in the legendary paintings of Gong Xian (the Qing dynasty) and Wang Wei (the Tang dynasty) will be discussed.

分会编号-34

以价值导向的文物保护行为研究——以古建筑保护为例

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本工作首先以浙江省古建筑文物为例，对文物价值进行了量化分析。文物价值是体现文物与一般构建筑物的本质区别，是文物保护领域的核心对象。对文物价值进行分类，分析几种主要的文物价值相互之间的逻辑关系，得出了“历史价值为基础、科学文化价值为重要核心、社会文化和经济价值为重要表现”的价值结构关系。

历史上多次修缮以及修缮时采用的新材料，会对文物的历史价值造成损害。但由于及时得到修缮，消除了古建筑文物短期内坍塌的危险，因此对文物价值整体而言，修缮行为是积极和必要的。古建筑上的每一种材料都有自身独特的劣化规律，将这些规律结合突发灾害的概率进行总结，可以得到古建筑文物价值的衰减曲线。

基于“日常保养+应急保护+修缮工程”相结合的保护手段，分析了预防性保护后古建筑文物价值得到改善的规律。本工作利用模型测算出了预防性保护前后浙江省古建筑文物在修缮间隔、坍毁几率和修缮成本方面的明显区别。

本工作采用价值量化后数据分析的方法，以图像的方式表现出了预防性保护措施的意义与价值。预防性保护对古建筑文物的好处主要在于，延长古建筑修缮间隔周期，减少突发灾害造成破坏，增强对抗材料劣化影响能力，节约保护投入的人力与物力。

分会编号-35

In-situ growth of enamel-like hydroxyapatite coating for marble conservation

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Outdoor stone relics including buildings, statues, temple Grottoes, etc., are continuously subjected to natural weathering and air pollutants. Those made of marbles and other carbonate rocks are particularly vulnerable to acid rains, which can be protected by acid-resistant coatings. A novel method to prepared enamel-like hydroxyapatite

coating on marble surface is presented in this paper and in-situ analyzed by optical microscopy, scanning electronic microscope, grazing incident X-ray diffraction and nano-indentation. The described coating is composed of tightly arranged rod hydroxyapatite nanocrystals perpendicular to the marble substrate with a thickness of 3-5μm. Not only does the coating exhibit high acid resistance, but it also has considerably higher elastic modulus and hardness compared to that synthesized by the well-known diammonium phosphate (DAP) method owing to the well-arranged microstructure. Consequently, the enamel-like hydroxyapatite coating would be probably more effective and durable for marble protection than the existing calcium phosphate coating.

分会编号-36

Multiple exciton generation effect enhanced photocatalyst for overall water splitting

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Multiple exciton generation (MEG), where two or more electron–hole pairs are produced from the absorption of one high-energy photon, could increase the efficiency of light absorbing devices. However, demonstrations of the effect are still scarce in photocatalytic hydrogen production. Moreover, many photocatalytic systems for overall water splitting suffer from poor charge carrier separation. Here we show that a CdTe quantum dot/vanadium-doped indium sulphide (CdTe/V-In_2S_3) photocatalyst has a built-in electric field and cascade energy band structure sufficient to effectively extract excitons and separate carriers, allowing MEG to be exploited for hydrogen production. We achieve a tunable energy band structure through quantum effects in CdTe and doping engineering of V- In_2S_3, which induces a 14-fold enhancement in the CdTe/V-In_2S_3 interfacial built-in electric field intensity relative to pristine CdTe/V- In_2S_3. We report an internal quantum efficiency of 114% at 350 nm for photocatalytic hydrogen production, demonstrating the utilization of MEG effects. The solar-to-hydrogen efficiency is 1.31%.

分会编号-37

In situ photocatalytically enhanced thermogalvanic cells for electricity and hydrogen production

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High-performance thermogalvanic cells have the potential to convert thermal energy into electricity, but their effectiveness is limited by the low concentration difference of redox ions. We report an in situ photocatalytically enhanced redox reaction that generates hydrogen and oxygen to realize a continuous concentration gradient of redox ions in thermogalvanic devices. A linear relation between thermopower and hydrogen production rate was established as an essential design principle for devices. The system exhibited a thermopower of 8.2 millivolts per kelvin and a solar-to-hydrogen efficiency of up to 0.4%. A large-area generator (112 square centimeters) consisting of 36 units yielded an open-circuit voltage of 4.4 volts and a power of 20.1 milliwatts, as well 0.5 millimoles of hydrogen and 0.2 millimoles of oxygen after 6 hours of outdoor operation.

分会编号-38

The proper encapsulation design of MOFs regulates carrier separation for efficient photocatalytic overall water splliting

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Photocatalytic water splitting is a potential technology to boost the development of renewable energy. However, carrier separation is difficult and the reverse recombination is severe during photocatalysis, resulting in a low overall

water splitting efficiency. Improving photocatalytic performance by regulating carrier migration behavior is a difficult problem to be solved urgently in this field. Our previous studies have shown that the carrier transport path can be modified by encapsulation strategies of MOFs, but the designs are not detailed enough. Motivated by this, we propose the research idea of applying the fine packing design of MOFs to the photocatalytic water splitting of hydrogen and oxygen production. In this proposal, we will investigate the controllable fabrication of novel MOF photocatalysts, realize the efficient construction of MOF encapsulated catalysts TiO2 and electron complement Au, and explore the formation laws of the encapsulated structures. The correlation between the optical response of the composite catalyst and the carrier transport characteristics at the catalytic site is clarified through the study on the photoelectric properties. The structure-activity relation between encapsulation structure, optical absorption, electrical effects, and photocatalytic properties is established through the evaluation of photocatalytic properties, and the stability of composite photocatalysts are explored. Based on the above, the mechanism by which the reasonable design of MOFs enhances the overall water splitting performance is clarified. The improved encapsulation will provide a novel idea for obtaining high-efficiency photocatalytic overall water splitting catalysts.

分会编号-39

Combating Mold and Insect Infestation: Unveiling a Novel Archive Packaging

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Archives, ancient books, calligraphy, painting, and other cultural classics constitute vital tangible material cultural heritages that encapsulate historical, cultural, and spiritual wealth. Over time, these cultural classics have suffered significant deterioration due to environmental factors and the actions of organisms. In response to the challenges posed by mold growth and insect infestation during the preservation of archives and ancient books, this project proposes the development of a hybrid paper coating that incorporates diverse inorganic nanomaterials. Through improving the antimicrobial efficiency and adjust the micro-environment, research packaging antimicrobial effect and mechanism on paper archives mildew. Firstly, the packaging should be constructed to study the paper affinity and environmental stability. Secondly, the antimicrobial and insecticidal efficiency and molecular mechanism of packaging will be elucidated. Further, the inhibition effect and regulatory mechanism of key signal molecules in packaging in various microorganisms and insecticidal would be analyzed. In the present study, inorganic and organic materials were introduced into the archive packaging box to alter the micro-environment and enhance the mould and fire prevention effect without affecting the paper performance. Archive packaging boxes have good anti-microbial and anti-insect effects, with a low content of carbon and nitrogen sources effectively blocking the growth and colonization of mould and insect, creating a micro-environment blocking the growth of surrounding mould, and significantly blocking the occurrence of fire, which could effectively improve storage capabilities and staff health in libraries.

分会编号-40

Preparation of a Nano Aluminum Phosphate Enhanced Hydroxyapatite Coating for Marble Conservation

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Open-air marble relics in Beijing are experiencing degradation due to sugaring, dissolution and other illnesses. Therefore, it is necessary to apply a protective and reinforcing coating to the weathered surface. Hydroxyapatite

(HAP) has significantly lower solubility and dissolution rate compared to calcite. Additionally, HAP has similar lattice parameters with calcite, suggesting that a cohesive layer of HAP can be formed over calcite. In fact, HAP exhibits a lattice mismatch of 5% with calcite, which might potentially lead to stress if the layer exceeds a few nanometre in thickness. On the other hand, aluminum phosphates (ideally, B-$AlPO_4$) only exhibit a 1% mismatch with calcite and have a solubility lower than that of calcite. In this study, in order to improve the property of HAP in marble conservation, sol-gel method was employed to synthesise nano $AlPO_4$, which were then incorporated into the phosphate solution to produce protective coating on the stone surface. The coating's morphology and the structure were characterized by Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), high capacity 3D X-ray microscopy (XRM), optical microscope, and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). Moreover, the color, the contact angle, the three-point bending strength measurements, as well as the simulated acid rain test and freeze–thaw treatment were performed to assess the chromatic aberration, hydrophilicity, reliability, and durability of the coating. Results indicated that the nano $AlPO_4$, with its matched lattice parameters and nucleation site provision, facilitated the formation a coherent HAP layer of crystal flakes. Subsequently, the anti-corrosion property, freeze-thaw resistance and consolidation property of the coating were improved, demonstrating the potential application the hybrid of HAP with nano $AlPO_4$ in the preservation of marble.

分会编号-41

Preliminary study on hygroscopic swelling of Wooden cultural relics

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Wooden materials, with their widespread distribution and diverse types, are deeply intertwined with human civilization. Wooden cultural relics, including wooden objects, palm leaf manuscripts, bamboo slips and wooden tablets, hold immense historical, artistic, and social value. During burial, these relics undergo degradation, and upon excavation or exposure from water, changes in environmental humidity can cause severe dimensional changes, potentially leading to irreversible damage and affecting their longevity. Therefore, understanding the humidity response mechanism of wooden relics' dimensional stability is a critical focus for conservationists.

Traditional methods for evaluating the dimensional stability of wooden culture relics are labor-intensive, time-consuming, imprecise, and often fail to cover the relative humidity ranges in actual storage conditions. There is an urgent need for the development of devices and techniques capable of accurately measuring the hygroscopic swelling of wooden culture relics in three anatomical directions. This study aims to utilize a self-developed, humidity precisely controllable static Thermal Mechanical Analyzer (TMA) and a Dynamic Vapor Sorption (DVS) coupled with Digital Image Correlation (DIC) system to test the hygroscopic swelling rates of waterlogged archaeological wood from the Nanhai No.1 shipwreck and palm leaf manuscripts of Qing dynasty within relative humidity ranges of 0% to 98% and 0% to 95%, respectively.

The results indicate that: (1) The hygroscopic swelling rates in all three anatomical directions of waterlogged archaeological wood are higher than those of modern healthy wood of the same species. While the longitudinal hygroscopic swelling rate of modern healthy wood is 0.1% to 0.3%, with radial and tangential rates approximately 10 and 15 times higher, respectively, the degradation in archaeological wood leads to a significant increase in longitudinal swelling and a reduction in the differences among the three directions. (2) For moderately degraded waterlogged archaeological wood, the tangential hygroscopic swelling increases more significantly with moisture content than the radial swelling. However, in severely degraded samples, the increase in both radial and tangential swelling rates with moisture content is nearly identical. (3) Palm leaf manuscript samples exhibit a greater

hygroscopic swelling in the transverse direction compared to the longitudinal direction.

墙报

分会编号-P01

Study on anti-weathering mechanism of earthen relics through weakening the reinforcement interface difference

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Traditional reinforcement through the information of solid layer or hydrophobic layer on soil surface enhances the strength of earthen relics. The problem is that the physical and chemical difference between solid layer or hydrophobic layer and soil is large. Under the impact of natural environment, the stress imbalance on both sides of the reinforced interface is the main reason for the formation of the diseases such as peeling, hollowing, cracking.

In order to decrease the interface difference above mentioned, ethanol aqueous with low dielectric constant was used as the carrying medium, and hydrolytic condensation product of siloxane was used as reinforcement agent. This reinforcement was dripped in simulated soil sample. The results shows that the original structure and composition of soil are remained after reinforcement. In addition, the anti-weathering of reinforced soil is better. Thus, it is proved that weakening the reinforced layer forms an obvious interface and reducing the difference of the interface stress between the reinforced layer and the cultural relic soil is the key to the durability anti-weathering reinforcement mechanism of soil remains.

分会编号-P02

透明类珠宝文物修复技术的研究

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透明类珠宝文物修复是当前文物修复保护的难题之一。由于该类文物透明度较高，因此对修复精度以及修复材料的透明度、渗透性等方面提出更高的要求。与之相对的是，当前透明类珠宝文物修复的研究较少，其修复往往仅是简单拼接，缺少一种可行的高精度修复方法和相应的修复材料。在文物修复理念的指导下，本工作以多种修复材料为样本，进行科学的模拟试验。 从对接紧密度、透明度、渗透性等角度对修复材料进行多次测试评估后发现，Hxtal NYL-1（海克斯塔）的效果最为理想。 而后，通过对比和研究当前破损文物的高精度修复方法，结合透明类珠宝文物特性，设计出一套以负压法原理为基础的透明类珠宝文物修复方法。 这种方法能够强化修复材料的渗透能力，解决粘接、补配中的定位问题，通过研磨膏的打磨、抛光，能够进一步消除修复痕迹。 最后，将这种修复方法和相应的修复材料成功应用于一件合浦汉墓出土的水晶、绿柱石串饰的修复，并达到了预期的修复效果，进一步验证了这种透明类珠宝文物修复方法的可行性和科学性。

分会编号-P03

33D/4D additive–subtractive manufacturing of ceramics for heritage restoration

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Additive manufacturing technology is gradually becoming a revolutionary tool in the research and

restoration of cultural heritage. Three-dimensional (3D) printing is able to accurately capture the form and details of cultural relics through high-precision digital scanning, and then print out the missing or damaged parts of the relics to achieve physical restoration. This non-contact method not only avoids secondary damage to fragile artefacts, but also improves the accuracy and efficiency of the restoration. 3D printing provides solutions to programmable constructing ceramic architectures. However, the development of ceramic printing is limited by geometrical complexity, structural resolution, manufacturing efficiency, material diversity, and low flexibility of heterogeneity. Four-dimensional (4D) printing technology further expands the scope of application by allowing the printed parts to undergo predetermined shape or functional changes under specific conditions (e.g. humidity, temperature changes), providing a new way of thinking about dynamic restoration and conservation of cultural heritage. Our work has developed the world's first 4Dprinting for ceramics and helps enhance the geometrical flexibility of ceramics, which has been listed by the European Commission as one of the 4D printing cases in "100 Radical Innovation Breakthroughs for the Future" (Guo Liu et al. Jian Lu*, Sci. Adv., 4, 8, eaat0641, 2018). A paradigm for a one-step shape/material transformation, high-2D/3D/4D-precision, high-efficiency, and scalable 4D additive–subtractive manufacturing (ASM) of shape memory ceramics has been developed (Guo Liu et al. Jian Lu*, Adv. Mater., 35, 39, 2302108, 2023). Furthermore, our work demonstrated flexible and rapid approaches for fabricating complicated and precise heterogeneous ceramics by shape-changing (4D) or shape-keeping (3D) ASM methods. The integration of subtractive manufacturing, including laser engraving/cutting/polishing, for a homogeneous precursor or heterogeneous precursors with the shape-changing/keeping strategy would contribute to complex-shaped and high-resolution 3D/4D printing of heterogeneous ceramics (Guo Liu, Xinya Lu, Xiaofeng Zhang et al. Jian Lu*, J. Mater. Sci. Technol., 201, 210-221, 2024). The proposed framework is expected to broaden the applications of structural ceramics in not only modern science (e.g., aerospace, biomedical, electronics) but also traditional arts (e.g., conservation and restoration of heritage restoration) (Xinya Lu, Guo Liu, Jian Lu*, Addit. Manuf. Front., invited review).